

DESCRIPTION**METHOD FOR PRODUCING SINGLE-WALLED CARBON NANOTUBES****TECHNICAL FIELD**

The invention of this application relates to a method for producing single-walled carbon nanotubes. More precisely, the invention of this application relates to a method for producing single-walled carbon nanotubes, which do not require a porous material or catalyst particles as a catalyst carrier and which enable production of single-walled carbon nanotubes with controlled diameter.

BACKGROUND ART

Heretofore, chemical vapor deposition (CVD) methods have been specifically given attention in production of high-quality single-walled carbon nanotubes (SWNTs), that are extremely useful in various industries. This is because CVD methods may enable industrial mass-production of SWNTs and have the potential for controlling the vapor phase thermal decomposition growth of SWNTs by skillfully controlling the type and the particle size of the catalyst to be used.

Many researchers have made various studies relating to the production of SWNTs through chemical vapor deposition, and some reports have been made by them. For example, J. King. et al. have reported that SWNTs can be obtained by heating to 1000°C a substrate coated with a mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mo}(\text{acac})_2$ and alumina nanoparticles in a methane gas

atmosphere. J. H. Hafner, et al. have reported that SWNTs grow when nanometer-size metal particles supported on alumina nanoparticles are heated with circulated CO gas. In these experiments, a salt of Fe and/or Mo is used as a metal-based catalyst, and alumina nanoparticles are used as the carrier.

There are other reports of production of SWNTs through chemical vapor deposition, reporting that use of porous material such as zeolite, silica or anodized silicon oxide as a carrier enables production of SWNTs.

However, it is to be noted that, when chemical vapor deposition is carried out without use of such nanoparticles or porous material as a carrier in the above-mentioned experiments, then SWNTs could not be formed but only multi-walled carbon nanotubes are obtained irrespective of the amount and the size of the metal-based catalyst used.

Specifically, in production of SWNTs through conventional vapor phase deposition, use of a metal-based catalyst and nanoparticles or porous material as a carrier of the metal-based catalyst is an indispensable requirement. Taking industrial mass-production of SWNTs into consideration, a substrate that has a fine structure comparable to that of nanoparticles or porous material and has a broad surface area will be needed as the carrier.

The invention of this application has been made in consideration of the above-mentioned situation, and its object is to provide a method for producing single-walled carbon nanotubes, which does not require nanoparticles and porous material as a carrier and which enables production of single-walled carbon nanotubes with controlled diameter.

DISCLOSURE OF THE INVENTION

To solve the above-mentioned problems, the invention of this application provides the following:

In the first aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, which comprises using a combination of a metal-based catalyst having a catalytic function in formation of graphite and a single-crystal substrate having a certain correspondence to the metal-based catalyst with respect to the crystal grain size and the crystal orientation thereof, dispersing the metal-based catalyst on the single-crystal substrate, and feeding a carbon material to the substrate at any temperature not lower than 500°C to thereby grow single-walled carbon nanotubes through vapor phase thermal decomposition.

In the second aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the single-crystal substrate is coated with a thin film of metal-based catalyst; in the third aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the thin film of metal-based catalyst has a thickness of from 0.1 to 10 nm; in the fourth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the metal-based catalyst is any one or a mixture of elements of a group consisting of iron group metals, platinum group metals, rare earth metals, transition metals, and their metal compounds; in the fifth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the single-crystal substrate is formed of a substance stable at 500°C or higher; in the sixth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the single-crystal substrate is sapphire (Al_2O_3), silicon (Si), SiO_2 , SiC, or MgO; in the seventh

aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein hydroxyapatite is used in place of the single-crystal substrate; in the eighth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein single-walled carbon nanotubes with controlled diameter are grown through vapor phase thermal decomposition, the diameter depending on the combination of the metal-based catalyst, the single-crystal substrate, and the crystal plane where the two contact; in the ninth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the combination of the metal-based catalyst, the single-crystal substrate, and the crystal plane where the two contact is a combination of Fe and the A-plane, R-plane or C-plane of sapphire; in the tenth aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the carbon material is a carbon-containing substance that is gaseous at any temperature not lower than 500°C; in the eleventh aspect thereof, the invention provides a method for producing single-walled carbon nanotubes, wherein the carbon material is methane, ethylene, phenanthrene, or benzene.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 includes photographs of SEM images, showing a deposit grown at 800°C on the A-plane (a), the R-plane (b) and the C-plane (c) of sapphire coated with a thin Fe film having a thickness of 2 nm.

Fig. 2 includes photographs of SEM images, showing a deposit grown at 800°C on the A-plane (a), the R-plane (b) and the C-plane (c) of sapphire coated with a thin Fe film having a thickness of 5 nm.

Fig. 3 includes photographs of TEM images, showing a deposit grown on (a) A (2 nm), (b) R (2 nm), and (c) C (5 nm).

Fig. 4 shows the Raman scattering spectrum of single-walled carbon nanotubes produced in Example; (a) indicate a range of up to 500 cm^{-1} , and (b) indicates a range of from 1200 to 1800 cm^{-1} .

BEST MODE FOR CARRYING OUT THE INVENTION

The invention of this application has the characteristics as above, and its embodiments are described hereinunder.

The method for producing single-walled carbon nanotubes of the invention of this application comprises using a combination of a metal-based catalyst that has a catalytic function in the formation of graphite, and a single-crystal substrate that has a certain correspondence to the metal-based catalyst with respect to the crystal grain size and the crystal orientation thereof, dispersing the metal-based catalyst on the single-crystal substrate, and feeding a carbon material to the substrate at any temperature not lower than 500°C to thereby grow single-walled carbon nanotubes through vapor phase thermal decomposition.

In the invention of this application, various types of metals having a catalytic function in formation of graphite, that is, in vapor phase thermal decomposition growth of single-walled carbon nanotubes, may be used for the metal-based catalyst. Concretely, for example, any one or a mixture of components of the group consisting of iron group metals such as Ni, Fe, Co; platinum group metals such as Pd, Pt, Rh; rare earth metals such as La, Y; transition metals such as Mo, Mn; and their metal compounds may be used

herein.

For the single-crystal substrate, any of various materials that are stable at the treatment temperature of 500°C or higher can be used. For example, they include sapphire (Al_2O_3), silicon (Si), SiO_2 , SiC, and MgO. In contrast to those in the related art, these materials are not always required to be porous structures or nanoparticles, and they may be flat. In the invention of this application, the single-crystal substrate may be replaced, for example by pillar crystals such as hydroxyapatite.

One characteristic feature of the invention of this application resides in the combination of the metal-based catalyst and the single-crystal substrate. In the invention of this application, the metal-based catalyst and the single-crystal substrate have a specific correspondence to each other. Specifically, the metal-based catalyst may be combined with the single-crystal substrate in such a manner that the substrate may act on the specific correspondence to the catalyst in point of the crystal grain size of the recrystallized grains thereof formed through solid-phase reaction such as deposition or recrystallization of the metal-based catalyst at the treatment temperature of 500°C or higher, and of the crystal orientation between the neighboring non-recrystallized grains. More concretely, for example, it is desirable that the single-crystal substrate may control the crystal grain size of the metal-based catalyst to fall within a range of from 0.1 to 10 nm or so, at the treatment temperature of 500°C or higher, and may have a relation with the metal-based catalyst which acts to make the crystal plane of the catalyst specifically oriented relative to the single-crystal substrate. One preferred embodiment of the combination of the metal-based catalyst and the single-crystal substrate in the invention of this application is a combination

of Fe and sapphire.

The mode of dispersing the metal-based catalyst on the single-crystal substrate is not specifically defined. For example, it may be realized by dispersing fine particles of a metal-based catalyst on a single-crystal substrate, or by coating a single-crystal substrate with a thin film of a metal-based catalyst. The latter method is preferred, as it is simple in actual production lines. Various methods may be utilized for the dispersion, concretely including, for example, a dry process of vacuum evaporation or sputtering, and a wet process of liquid-dropping, spraying or spin-coating.

The amount of the metal-based catalyst to be dispersed on the single-crystal substrate is not specifically defined, and may be any desired one. For example, the catalyst may be partially or wholly dispersed on the single-crystal substrate to a thickness of one atomic layer or so. When it is desired that the single-walled carbon nanotubes are obtained at a relatively high yield, then for example a metal-based catalyst is dispersed on a single-crystal substrate as a thin film thereof and the thickness of the film is controlled to fall within a range of from 0.1 to 10 nm or so, though this may not always be desirable depending on the combination of the metal-based catalyst and the single-crystal substrate. If the film of metal-based crystal is too thick, then it is unfavorable since the film may not be able to interact with the single-crystal substrate locally in some surface part thereof and, as a result, there may be a possibility that the metal-based catalyst particles cannot be controlled by the substrate.

The single-crystal substrate thus having the metal-based catalyst dispersed thereon is heated at any temperature not lower than 500°C, and then a

carbon material is fed to it.

Heating the single-crystal substrate to any temperature not lower than 500°C may be done in an inert atmosphere. The carbon material may be any of the carbon-containing substances that are gaseous at any temperature not lower than 500°C. More concretely, it includes, for example, methane (CH₄), ethylene (C₂H₄), carbon monoxide (CO) and others that are gaseous at room temperature; and phenanthrene, benzene and others that are solid or liquid at room temperature but become gaseous when heated at 500°C or higher. With it, single-walled carbon nanotubes may be grown on the surface of the single-crystal substrate through vapor phase thermal decomposition thereon.

When the metal-based catalyst and the single-crystal substrate are suitably combined in the manner as above, then single-walled carbon nanotubes may be produced, not requiring porous-structured or granular-shaped single-crystal substrates as in the related art.

Having noted the interaction between the metal-based catalyst and the single-crystal substrate in the invention of this application, we, the present inventors have made more detailed studies into this, and as a result have found that not only the combination of the metal-based catalyst and the single-crystal substrate as above but also the crystal plane of the single-crystal substrate should be taken into consideration in determining the interaction between the metal-based catalyst and the single-crystal substrate, and that the diameter of the single-walled carbon nanotubes to be formed may be specifically controlled depending on the combination of all the above. The technology of controlling the diameter of single-walled carbon nanotubes in producing them in a mode of vapor phase thermal decomposition growth thereof has not been known at all up

to now, and we, the present inventors, are the first to have realized it. Specifically, the method for producing single-walled carbon nanotubes which the invention of this application provides herein is characterized in that the specific combination of the metal-based catalyst, the single-crystal substrate, and its crystal plane connecting the two realizes vapor phase thermal decomposition growth of single-walled carbon nanotubes with a specific diameter.

More concretely, for example, for the preferred combination of metal-based catalyst and single-crystal substrate, Fe and sapphire mentioned above, the combination of Fe with any of the A-plane, R-plane or C-plane of sapphire may be taken into consideration, and the diameter of the single-walled carbon nanotubes to be formed through vapor phase thermal decomposition growth thereof may be controlled differently in every combination of these. For example, regarding the combination of Fe with the A-plane, R-plane or C-plane of sapphire, the diameter of the single-walled carbon nanotubes to be grown is controlled to specific values of 1.43 nm, 1.30 nm and 1.20 nm on the A-plane; 1.45 nm, 1.24 nm and 1.18 nm on the R-plane; and 1.49 nm, 1.31 nm and 1.18 nm on the C-plane.

In the invention of this application, in addition, the thickness of the thin film of metal-based catalyst may be controlled differently on each crystal plane of the single-crystal substrate and the yield of the single-walled carbon nanotubes to be produced may be thereby increased. More concretely, for example, regarding the combination of Fe with any of the A-plane, R-plane or C-plane of sapphire, the yield of the single-walled carbon nanotubes may be increased on the A-plane and the R-plane by reducing the thickness of the thin Fe film thereon within the range mentioned above, while the yield thereof to be

formed on the C-plane may be increased by increasing the thickness of the thin Fe film thereon within that range.

On the other hand, existence of single-walled carbon nanotubes of various symmetry (chirality) is known. The chirality of single-walled carbon nanotubes may be represented by chirality indexes (m, n) , and it has strong correlation with the diameter of the single-walled carbon nanotubes. This suggests the possibility that the method of the invention of this application may control not only the diameter but also the chirality of single-walled carbon nanotubes.

As described hereinabove, the invention of this application indicates that the interaction between the metal-based catalyst and the single-crystal substrate material plays an important part in vapor phase thermal decomposition growth of single-walled carbon nanotubes, and, when a single-crystal substrate with such a metal-based catalyst dispersed thereon is used, then single-walled carbon nanotubes may be grown through vapor phase thermal decomposition thereon. In addition, when the combination of the metal-based catalyst with the single-crystal substrate and its crystal plane is suitably selected, the diameter of the single-walled carbon nanotubes is controlled. Further, when the crystal plane of the single-crystal substrate and the thickness of the thin catalyst layer formed thereon are suitably controlled, then the yield of the single-walled carbon nanotubes to be formed on the substrate may be increased.

Example of the invention is described below with reference to the drawings attached hereto, and the embodiments of the invention are described in more detail.

EXAMPLE

Producing SWNTs was tried, using a tube furnace having an inner diameter of 2 inches and using methane gas as the carbon material. For the single-crystal substrate, the A-plane, R-plane and C-plane of sapphire were used. On the single-crystal substrate, a thin Fe film serving as the metal-based catalyst was formed through electron beam deposition in a vacuum of about 4×10^{-6} Torr so that its thickness would be from 2 to 5 nm.

These substrates were introduced into a tube furnace and heated in an argon atmosphere; and after they reached a predetermined temperature between 600°C and 800°C, methane (99.999 %) used here as the carbon material was fed thereinto at a flow rate of 0.6 liters/min. The methane introduction continued for 5 minutes, and then argon was again introduced into the furnace. Then, the tube furnace was cooled to room temperature.

After the heat treatment, the substrates were analyzed in detail through observation with a scanning electron microscope (SEM), through Raman spectrometry and through observation with a transmission electronic microscope (TEM). The samples for SEM observation were coated each with a thin Pd-Pt film having a thickness of about 2 nm for more definite observation thereof. For Raman spectrometry, the samples were exposed to 488 nm light (30 mW) from an Ar laser having a convergent spot size of about 1 μm . The samples for TEM observation were prepared by collecting the deposit from the sapphire substrate, dispersing it in ethanol, dropwise applying the resulting dispersion onto a TEM grid and drying it thereon.

<SEM Observation>

Fig. 1(a)(b)(c) show SEM images of the deposit grown at 800°C on the

A-plane, R-plane and C-plane, respectively, of sapphire coated with a thin Fe film having a thickness of 2 nm. It is definitely observed that the amount of the tubular deposit on the A-plane is larger than that on the R-plane. In addition, it is also clear that the amount of the tube deposit on the C-plane is the smallest of the three.

Fig. 2(a)(b)(c) show SEM images of the deposit grown at 800°C on the A-plane, R-plane and C-plane, respectively, of sapphire coated with a thin Fe film having a thickness of 5 nm. It is confirmed that the same tubular deposit as in the above is formed on all the three planes. It is understood that these nanotubes are either thick and short ones (having a diameter of from 20 to 50 nm and a length of about 1 μ m), or thin and long ones (having a diameter of less than 3 nm and a length of 2 μ m or more).

In addition, when the sapphire coated with a thin Fe film having a thickness of 2 nm was heated at 600°C, then hardly any tubular deposits grew on the A-plane and the R-plane of the substrate, but a few thicker nanotubes (having a diameter of from about 30 to 50 nm) were found to have grown on the C-plane. The structure of these nanotubes was analyzed through TEM observation and Raman spectrometry thereof.

<TEM Observation>

Fig. 3(a) shows a TEM image of the deposit grown on the A-plane of sapphire coated with a thin Fe film having a thickness of 2 nm (this is hereinafter indicated by A (2 nm)). It is understood that A (2 nm) includes SWNTs and an extremely small amount of amorphous carbon (this is hereinafter indicated by a-C). The TEM image of the deposit grown on the R-plane of sapphire coated with a thin Fe film having a thickness of 2 nm (this is

hereinafter indicated by R (2 nm)), shown in Fig. 3(b), confirms that R (2 nm) includes SWNTs and a-C. The TEM image of the deposit grown on the C-plane of sapphire coated with a thin Fe film having a thickness of 5 nm (this is hereinafter indicated by C (5 nm)), shown in Fig. 3(c), confirms that the amount of a-C is the largest on C (5 nm) and there are hardly any SWNTs. Though not shown in Fig. 3(c), it is confirmed that on C (5 nm) some double-walled carbon nanotubes were grown.

The TEM observation confirms that the diameter of SWNTs bundled on the A-plane, R-plane and C-plane of the substrate falls approximately between 1.0 and 1.7 nm.

<Raman Spectrometry>

Fig. 4(a)(b) show the Raman scattering spectrum of the deposit formed on the A-plane, R-plane and C-plane of sapphire coated with a thin Fe film having a thickness of 2 nm, 3 nm or 5 nm. All the samples showed peaks at about 1592 cm^{-1} and 1570 cm^{-1} , and showed from 1 to 4 fine peaks within a range of from 100 to 230 cm^{-1} . These peaks are characteristics of SWNTs, and indicate the presence of SWNTs in the deposit. The peaks appearing at about 1592 cm^{-1} and 1570 cm^{-1} correspond to the tangent mode, and the peaks appearing between 100 and 230 cm^{-1} correspond to Raman breathing mode (RBM) of the SWNTs.

For example, SWNTs formed on R (2 nm) gave a strong RBM peak at 167 cm^{-1} indicating that these are SWNTs having a diameter of 1.4 nm, and gave a weak peak at 203 cm^{-1} indicating that these are SWNTs having a diameter of 1.2 nm. However, it was found that the peaks given by the samples coated with an Fe film thicker than this are not pronounced. Thus, it is concluded from the

tangent mode and RBM mode peak intensity data that, with the increase in the thickness of the Fe film from 2 nm to 5 nm, the amount of SWNTs formed on the A-plane and the R-plane decreases. On the other hand, however, it is found that the amount of SWNTs formed on the C-plane increases with the increase in the thickness of the Fe film from 2 nm to 5 nm.

The peak position and the RBM intensity of these SWNTs differ among individual deposits thereof at different positions. Each deposit was more carefully analyzed in at least 10 different points thereof, and, as a result, the following tendency was clear. Specifically, the RBM peak width is narrow, falling between 7 and 12 cm^{-1} ; the number of the peaks is from 1 to 4; and the peak position depends on the plane of the substrate sapphire.

More concretely, for example, the Raman spectra obtained at 10 sites on the A-plane (2 nm), the R-plane (2 nm) and the C-plane (2 nm) were separately averaged, and the RBM peak and the calculated diameter of SWNTs are shown in Table 1.

Table 1

Sample	RBM Peak (cm^{-1})		
	SWNTs diameter (nm)		
A (2 nm)	170	188	203
	1.43	1.30	1.20
R (2 nm)	168	194	207
	1.45	1.24	1.18
C (2 nm)	164	186	206
	1.49	1.31	1.18

As in the above, when the crystal plane of the sapphire substrate is specifically selected, then SWNTs can be formed thereon with their diameter controlled to be a specific value.

(Comparative Example 1)

In place of the substrate sapphire in the above-mentioned Example, a silicon single-crystal plane (or SiO_2 plane thermally grown on silicon) was used, but SWNTs could not be formed thereon through CVD at 800°C irrespective of the thickness of the thin Fe film formed thereon.

(Comparative Example 2)

A sapphire substrate was coated with a thin Ni film in place of the thin Fe film as in the above-mentioned Example, and then processed in the same manner as above. However, SWNTs could not be formed on it.

(Comparative Example 3)

A silicon wafer with a mixture of $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and alumina nanoparticles (with no $\text{Mo}(\text{acac})_2$) applied thereto was prepared as a substrate. This was subjected to the same heat treatment as in the above-mentioned Example, and SWNTs were formed on it. The Raman spectrum of these SWNTs is shown in Fig. 4. The RBM peak of the Raman spectrum is broad, falling between 120 and 200 cm^{-1} , and this means that the diameter of SWNTs formed herein varies to fall within a broad range of from 1.2 to 2.0 nm .

From this, it is understood that, though the alumina nanoparticles of the metal-based catalyst carrier are formed of Al_2O_3 , the same as that of sapphire, the alumina nanoparticles have various crystal planes and amorphous characteristics because of their morphology, and therefore, SWNTs could grow thereon but the diameter of SWNTs grown thereon could not be controlled, and, as a result, the diameter of SWNTs grown thereon fell within a broad range.

Because of the reasons above, the production of SWNTs in conventional vapor phase thermal decomposition growth on a catalyst carrier unavoidably requires a porous material and nanoparticles as the catalyst carrier. In the

invention of this application, however, when the crystal to be the substrate, the crystal plane of the substrate, the metal-based catalyst, the film thickness of the catalyst and the crystal growing temperature are suitably selected, then SWNTs may be formed even on a flat crystal substrate. Accordingly, it is surmised that these requirements stipulated by the invention have influence on the catalyst metal diffusion coefficient and on the crystal grain size and the crystal orientation of the catalyst metal incidental to it, and, as a result, SWNTs having a specific diameter may be formed on the substrate.

Needless-to-say, the invention is not limited to the embodiments described hereinabove, and its details may undergo various changes and modifications.

INDUSTRIAL APPLICABILITY

As described in detail hereinabove, the invention relates to a method for producing single-walled carbon nanotubes. More precisely, the invention of this application provides a method for producing single-walled carbon nanotubes, which does not require a porous material and catalyst particles and which enables production of single-walled carbon nanotubes with controlled diameter.